TEMASEK JUNIOR COLLEGE

2023 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME		CG	/ 22
CENTRE NUMBER	☐☐☐☐	INDEX NUMBER	☐☐☐☐

CHEMISTRY **9729/03**

Paper 3 Free Response **14 Sep 2023**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre/index number, name, CG and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be shown clearly.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use			
Section A	**Q1**		
	Q2		
	Q3		
Section B (Circle one)	**Q4**	**Q5**	
TOTAL			**/ 80**

This document consists of **30** printed pages and **2** blank pages.

Section A

Answer **all** the questions in this section.

1 The transition metals such as iron and rhodium are known for their catalytic activity.

(a) The reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.

(i) Write the electronic configuration for iron(II) ions. [1]

(ii) Explain why the reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow. [1]

(iii) Explain why the iron(II) ions can be described as a *homogeneous catalyst*. [2]

(iv) State the property, typical of transition metals, which allows iron(II) ions to behave as a catalyst in this reaction.

Include relevant chemical equations to support your answer. [3]

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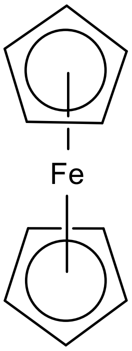
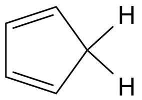
(b) Ferrocene is a highly stable compound in which the iron(II) ion is located between two cyclopentadienyl anion rings. Studies have shown that the carbon–iron bonding in ferrocene is capable of free rotation.



Ferrocene

(i) Suggest an alternative structure of ferrocene. [1]

The methylene hydrogen atoms shown in cyclopentadiene below are acidic. Cyclopentadiene can dissociate a proton to form the cyclopentadienyl anion.

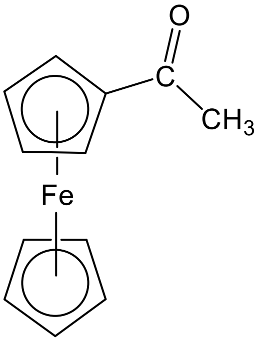


cyclopentadiene

(ii) Write an expression for the acid dissociation constant, K_a, for cyclopentadiene. [1]

(iii) Suggest the number of delocalised π electrons in the cyclopentadienyl anion. [1]

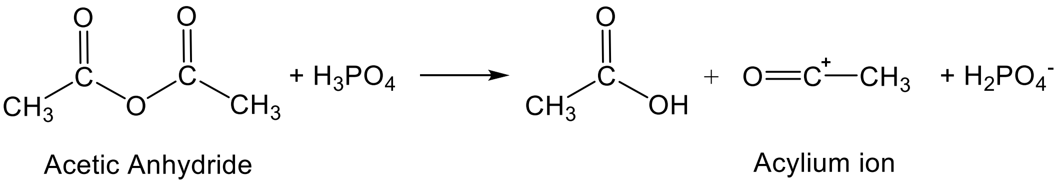
(iv) Similar to benzene, ferrocene undergoes electrophilic substitution with acetic anhydride and phosphoric acid to form the compound **W**.



compound **W**

The steps of the mechanism are as described.

Step 1: Acetic anhydride and phosphoric acid react to form the acylium ion.

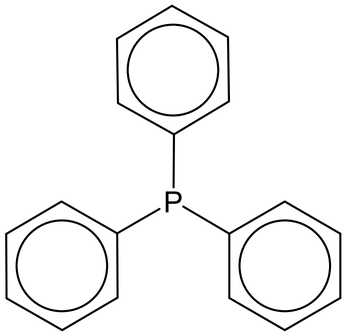


Step 2: Addition of the acylium ion to one of the carbon atoms on the cyclopentadienyl *anion* ring in ferrocene forms an intermediate.

Step 3: Loss of a proton from the intermediate to form **W**.

Suggest the mechanism for steps 2 and 3. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

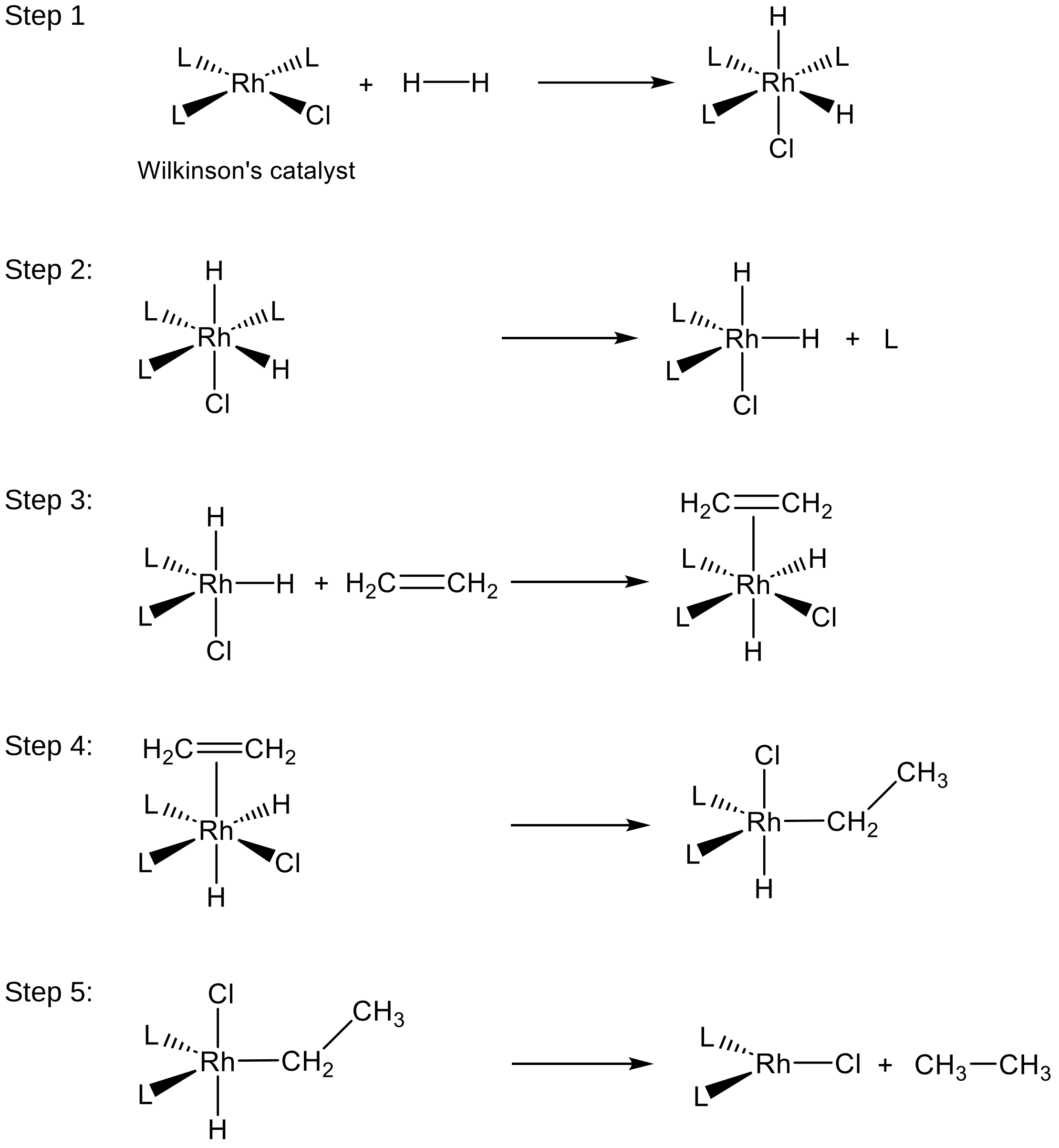
(c) Hydrogenation of alkenes can be catalysed by the rhodium (Rh)-containing catalyst, Wilkinson's catalyst, RhL_3Cl, where L is the triphenylphosphine ligand.



triphenylphosphine

(i) Explain using bonding why triphenylphosphine is insoluble in water. [2]

The following steps take place when Wilkinson's catalyst is used to carry out the hydrogenation of ethene. Hydrogen is reduced to hydride in step 1.



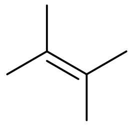
With consideration of the oxidation state at the Rh metal centre,

(ii) identify the step which involves an oxidative addition. [1]

(iii) identify the step which involves a reductive elimination. [1]

(iv) Step 4 of the reaction is the rate-determining step.

Suggest why the rate of reaction is slower when 2,3-dimethylbut-2-ene is used in place of ethene. [1]



2,3-dimethylbut-2-ene

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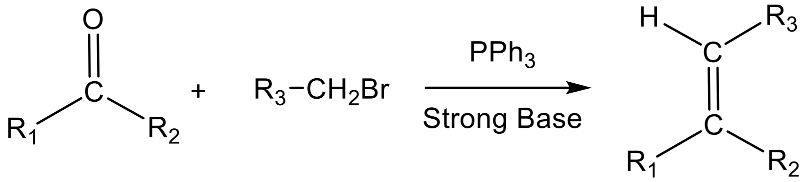
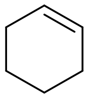
(d) Triphenylphosphine, PPh_3, is used as nucleophile in the Wittig reaction.

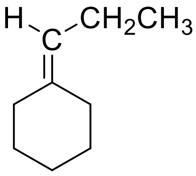
In the Wittig reaction, a carbonyl compound reacts with a halogenoalkane to form an alkene. The conversion is shown in the following unbalanced equation.



Suggest a three-step synthesis involving the Wittig reaction to convert cyclohexene to compound **Q**. [3]



cyclohexene



compound **Q**

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2 This question involves various components found in different types of aerosol propellants and sprays.

(a) Dimethylether, CH_3OCH_3, is a colourless gas that is used as an aerosol propellant.

Dimethylether can react with carbon dioxide to form carbon monoxide and hydrogen, as shown by the equation below.

$$CH_3OCH_3(g) + CO_2(g) \rightleftharpoons 3CO(g) + 3H_2(g) \qquad \Delta H = +245 \text{ kJ mol}^{-1}$$

(i) Write an expression for the equilibrium constant, K_p, for this reaction. Give the units for K_p. [2]

In an experiment conducted at 550 K, a mixture of CH_3OCH_3 and CO_2 was introduced into in a 2 m^3 sealed vessel. The initial total pressure was 12 atm at this temperature. The reaction was allowed to reach dynamic chemical equilibrium.

(ii) At equilibrium, the amount of CO was found to be 278.5 mol. Using the *ideal gas equation*, verify that the equilibrium partial pressure of CO in the vessel was 6.3 atm. [1]

(iii) At equilibrium, it was found that 70% of the CH_3OCH_3 had dissociated.

Calculate the equilibrium pressures of CH_3OCH_3 and CO_2 in atm. [3]

(iv) Hence, calculate the value of K_p, for this reaction. [1]

(v) Using a value of K_p of 12 Pa, determine the value of ΔG for this reaction and hence, comment on the significance of the sign of ΔG, in relation to the equilibrium composition at 550 K. [2]

(vi) Explain the effect (if any) on the average M_r of the reactants in the equilibrium mixture value when the experiment was conducted at 300 K instead of 550 K. [2]

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(b) An important property of an aerosol propellant is that it should be a gas at room temperature and pressure.

(i) State **three** assumptions of the kinetic theory as applied to an ideal gas. [3]

(ii) Fig. 2.1 illustrates the behaviour of 1 mol of ideal gas as well as 1 mol of CH_3OCH_3 at 293 K.

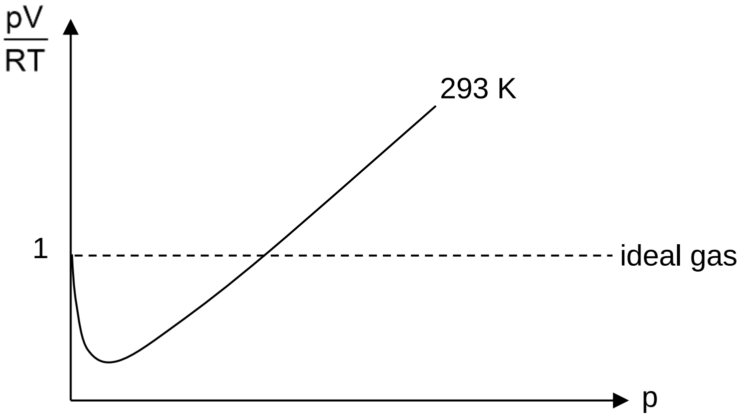

Fig 2.1

On the **same** axes in Fig. 2.1, sketch and label the graph for 1 mol of CH_3OCH_3 at 550 K. Explain your answer. [2]

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(c) Aerosol sprays containing copper(II) ions were used near a well. Copper(II) hydroxide deposits was observed in the well water.

The value of the solubility product, K_{sp}, of copper(II) hydroxide is 1.80×10^{-19} at 25°C.

The MCL is the maximum concentration of a contaminant in drinking water beyond which the water is not safe for consumption. The MCL for copper(II) ions is 1.3 mg dm^{-3}.

Determine if a water sample found in the well whose pH was found to be 7.75, is safe for consumption. [2]

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(d) Calcium fluoride is a component of aerosol spray and aids in the treatment of muscular tension and torn ligaments.

The data in Table 2.1 will be useful in this question.

Table 2.1

Lattice energy of CaF_2(s) / kJ mol^{-1}	–2640
Standard Gibbs free energy of solution of CaF_2(s) / kJ mol^{-1}	+64.4
Standard enthalpy change of hydration of Ca^{2+}(g) / kJ mol^{-1}	–1579
Standard enthalpy change of hydration of F^{-}(g) / kJ mol^{-1}	–524

(i) Define the term *standard enthalpy change of solution,* $\Delta H^{\ominus}_{\text{solution}}$, of CaF_2. [1]

(ii) Construct a labelled energy cycle to calculate the standard enthalpy change of solution of CaF_2. [2]

(iii) Hence, calculate the standard entropy change of solution, $\Delta S^{\ominus}_{\text{solution}}$, of CaF_2. [1]

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3 This question is about nitrogen compounds and its reactions.

(a) Nitric acid, HNO_3, is used as the main reagent for nitrating aromatic compounds such as benzene, phenylamine and phenol.

The table below shows the different conditions used for the mononitration of benzene, phenylamine and phenol.

	benzene	phenylamine	phenol
Reagents	mixture of concentrated HNO_3 and concentrated H_2SO_4	dilute HNO_3	dilute HNO_3
Temperature / ^{o}C	60	20	40

(i) Explain the need for concentrated H_2SO_4 in the nitration of benzene, but not for phenylamine and phenol. [2]

(ii) With reference to the data in the table above, comment on the difference in reactivity between phenylamine and phenol towards nitration. [2]

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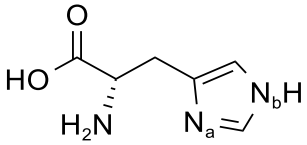
(b) Histidine is a naturally occurring amino acid which is used for repairing damaged tissues and making blood cells.

The structure of the histidine is shown below.



The 2 nitrogen atoms in the ring are sp^2 hybridised.

(i) Explain why nitrogen atom N_b does not have a pK_b value. [1]

(ii) The pK_b value for nitrogen atom N_a is 8.0.

In terms of hybridisation of nitrogen atom, explain why N_a is more basic than N_b. [1]

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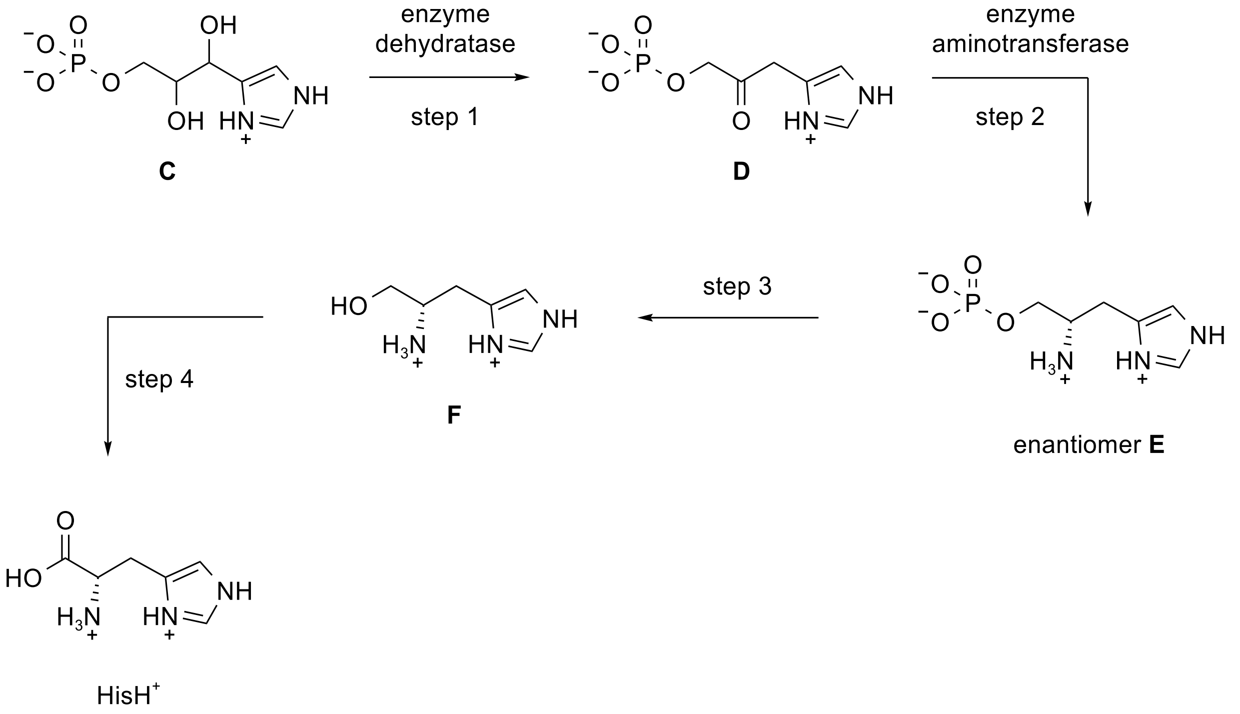
(c) The fully protonated form of histidine, HisH$^+$, can be synthesised from the reaction scheme below.

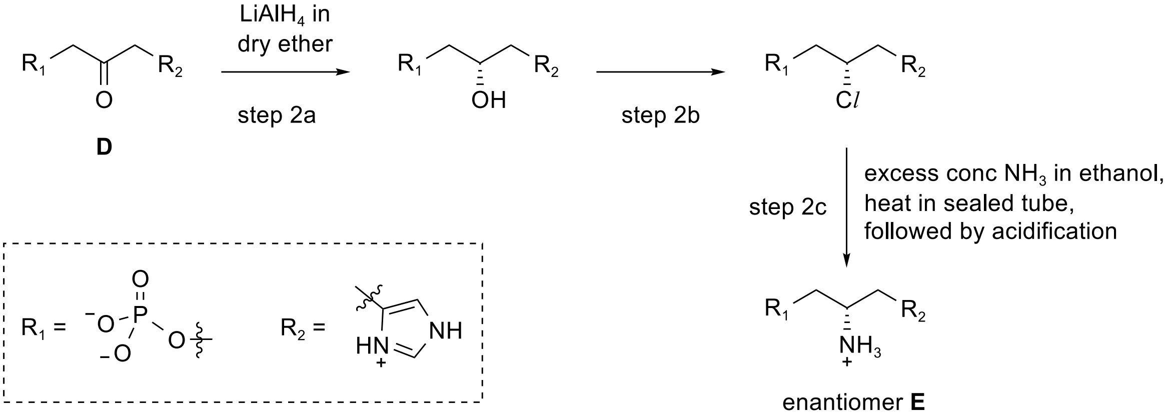


(i) Different stereoisomers have different biological properties towards enzymes.

It was found that only 25% of compound **C** could be converted to **D** by the enzyme dehydratase in step 1. Suggest an explanation for this observation. [2]

(ii) A student attempted to convert compound **D** to enantiomer **E** without the use of enzymes and proposed the following sequence of reactions.

D and **E** are represented by their simplified structures below.



By considering the stereochemical outcome of each step, explain why each of the following steps is **not** suitable to produce a good yield of enantiomer **E**. [2]

- Step 2a
- Step 2c

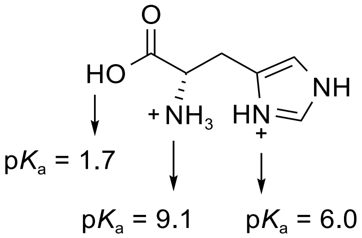
[Given that Step 2c follows a second order kinetics reaction]

(iii) HPO$_4$$^{2-}$ is obtained as a side product of step 3.

Suggest the type of reaction for step 3. [1]

(iv) State the reagent and condition needed to convert **F** to $HisH^+$ in step 4. [1]

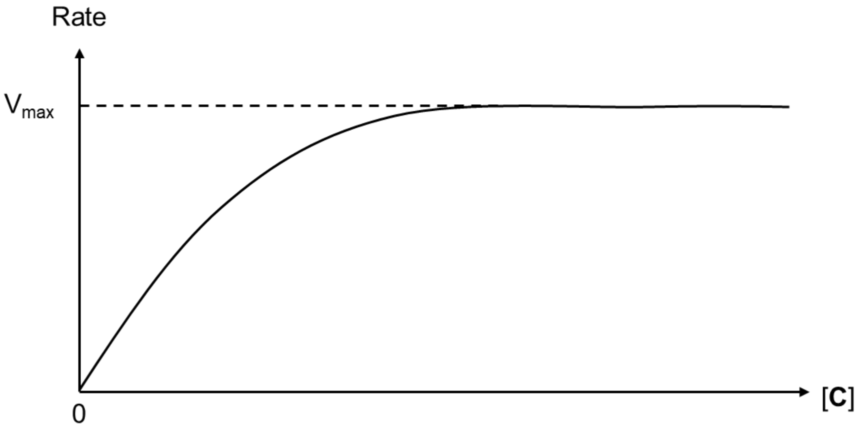
(v) The pK_a values for the fully protonated form of histidine, $HisH^+$, are shown below.



After step 4, $HisH^+$ is extracted, purified and transferred into a buffer solution at pH 7.55 for storage.

Draw the structure of the predominant species of histidine at this pH. [1]

(d) The kinetics of the reaction of step 1 was studied using different concentration of **C** with the enzyme dehydratase and the following graph is obtained.



(i) Explain fully the shape of the graph with respect to the order of reaction at low, moderate and high concentration of **C**. [3]

The Michaelis-Menten equation is used to analyse the kinetics of an enzyme-catalysed reaction. At low concentration of **C**, the equation simplifies to:

$$\text{Rate} = \frac{V_{max}}{K_M} \times [\textbf{C}]$$

where K_M is the Michaelis constant.

Under certain conditions, the K_M is 2.60×10^{-5} mol dm^{-3} and V_{max} is 10.4 mol dm^{-3} s^{-1} for step 1.

(ii) Using your answer in **(d)(i)** at low concentration of **C**, determine a value for the rate constant, *k* and hence the value of the half-life for step 1. [2]

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[Total: 18]

Section B

Answer **one** question from this section.

4 Chalcopyrite, $CuFeS_2$ and similar sulfide ores are the most common ores of copper. The ores typically contain low percentages of copper and have to be concentrated before refining.

In the extraction of copper, the mineral is smelted by heating with air. The equation for this reaction is as follows.

$$8CuFeS_2 + 21O_2 \rightarrow 8Cu + 4FeO + 2Fe_2O_3 + 16SO_2$$

(a) A sample of rock contains 1.30 % by mass of chalcopyrite. Assuming this is the only source of copper in the rock, calculate the percentage by mass of copper in the sample. [1]

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(b) The copper obtained during the smelting process may contain impurities such as zinc and silver. It is then refined using electrolysis.

Draw a well-labelled set-up for the electrolysis process and explain, using relevant data from the *Data Booklet*, how each of the two impurity metals is removed from the copper. [4]

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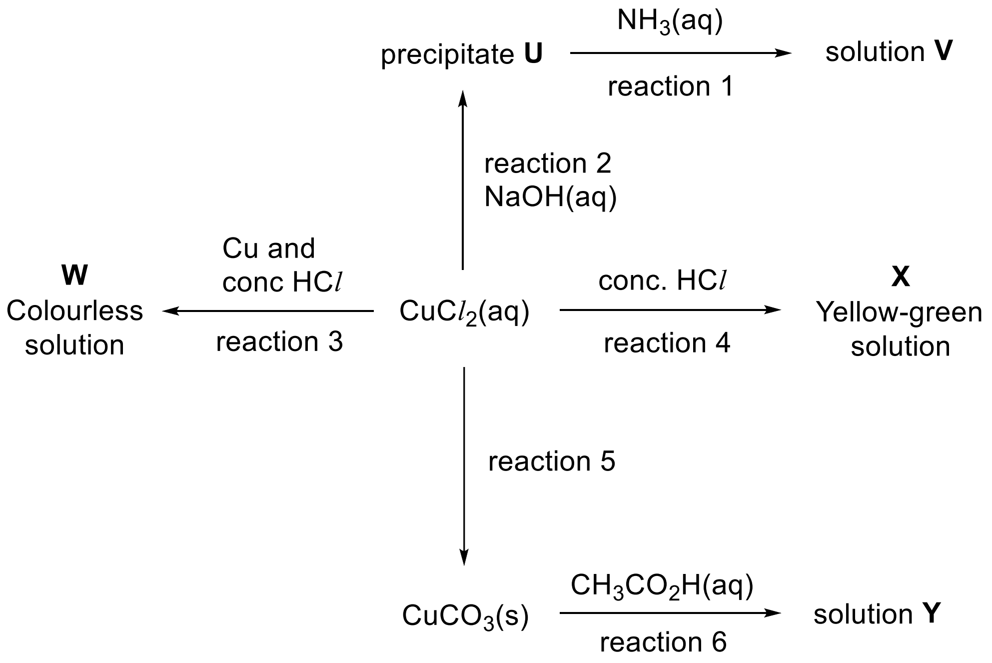
Copper is a transition element and it can form many complexes.

(c) The reaction scheme shows some reactions of copper and its compounds.



(i) Write the formulae of **U, V, W and X.** [2]

(ii) Identify a suitable reagent for reaction 5. [1]

(iii) Write the equation for reaction 6. [1]

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(d) Copper can form complexes with the ligands ammonia and ethane-1,2-diamine (en), $H_2NCH_2CH_2NH_2$, as shown below.

equilibrium 1

$[Cu(H_2O)_6]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 3.98 \times 10^{10}$

equilibrium 2

$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 5.01 \times 10^{7}$

(i) Write an expression for the equilibrium constant, K_{stab}, for equilibrium 2. State its units. [1]

(ii) The standard entropy change, $\Delta S^{\ominus}$, for equilibrium 1 is + 23 J K^{-1} mol^{-1} and for equilibrium 2 is – 8.4 J K^{-1} mol^{-1}. Suggest an explanation for this difference by reference to both equilibria. [2]

(iii) Of the three copper complexes in equilibria 1 and 2, state the formula of the copper complex that is the most stable and explain your choice. [1]

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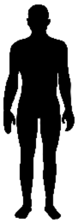
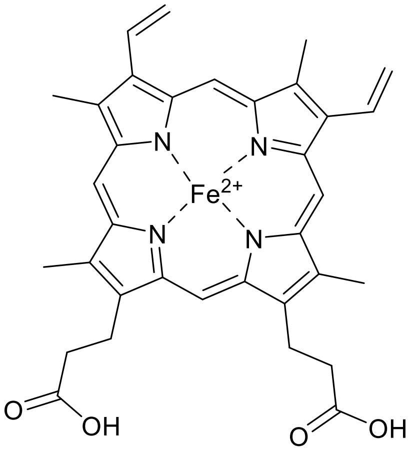
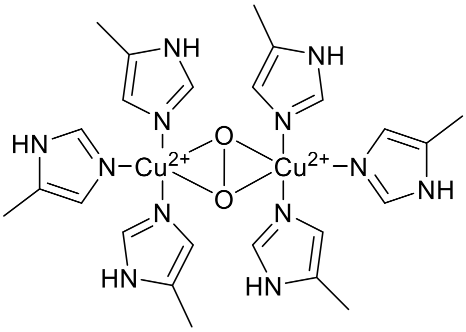
(e) Transition element complexes can exhibit stereoisomerism.

(i) Name the type of isomerism exhibited by $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and draw the three-dimensional diagrams of the two isomers. [2]

The diagram below shows the complexes present in human and spider blood.

Animal	Complex ion	Colour of blood
 Human	 haemoglobin	Red
 Spider	 oxyhaemocyanin	Blue

(ii) Explain, in terms of d-orbital splitting, why the colour of spider blood is blue while human blood is red. [2]

[Turn over

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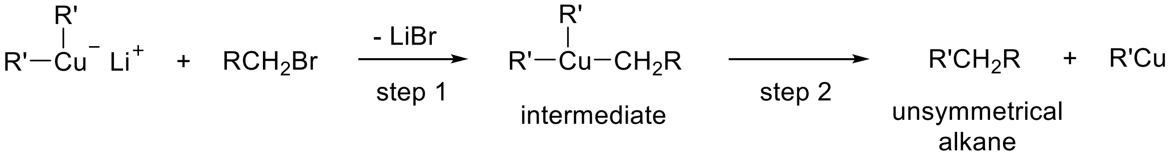
(f) An important compound of copper is copper(I) iodide which is used to prepare the Gilman reagent.

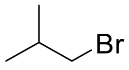
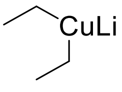
$$2R'Li + CuI \longrightarrow R'_2CuLi + LiI$$

Gilman
reagent

This reagent undergoes S_N2 reaction with primary halogenoalkanes to form the intermediate in Step 1. This synthetic method can be used to prepare unsymmetrical alkanes as shown below.



(i) Describe the mechanism for the formation of the intermediate. [2]

(ii) Predict the product formed when  reacts with . [1]

[Total: 20]

5 Use of the *Data booklet* is relevant to this question

(a) Nickel is a transition element with a variety of uses.

(i) Explain what is meant by the term *transition element*. [1]

(ii) Explain why the first ionisation energies of first row transition elements are relatively invariant. [2]

(iii) Suggest why the melting point of nickel is significantly higher than the melting point of calcium. [2]

(b) Nickel-Metal hydride (Ni-MH) battery is a rechargeable battery that has a cathode made up of NiO(OH) and an anode made up of hydrogen absorbed within a metal alloy represented as MH.

When the battery discharges, solid metal alloy, M, is formed at the anode and solid nickel (II) hydroxide, $Ni(OH)_2$ is formed at the cathode. The electrolyte is potassium hydroxide. The standard reduction potential of MH/M is –0.83V.

(i) Construct an equation, including state symbols, for the reactions at the cathode and anode. [2]

(ii) The cell is capable of producing an e.m.f of 1.32 V.

Suggest a value for the standard reduction potential of $NiO(OH)/Ni(OH)_2$. [1]

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(c) Nickel can form complexes.

(i) Suggest a reason for the difference between the following redox potentials. [1]

$Ni^{2+} + 2e \rightleftharpoons Ni$ $E^\ominus = -\,0.25$ V

$[Ni(NH_3)_6]^{2+} + 2e \rightleftharpoons Ni + 6NH_3$ $E^\ominus = -\,0.51$ V

.

Nickel forms many complexes in which the central atom is surrounded by four ligands.

The complex **X**, $[Ni(R_3P)_2I_2]$, exists as two isomers, one of which has a net dipole moment.

The complex **Y**, $[Ni(R_3P)_2Cl_2]$, exists as only one structure.

[R_3P is a monodentate ligand where R is CH_3]

(ii) Draw the structure of **Y** and the two isomers of **X**. Label your diagrams clearly. [2]

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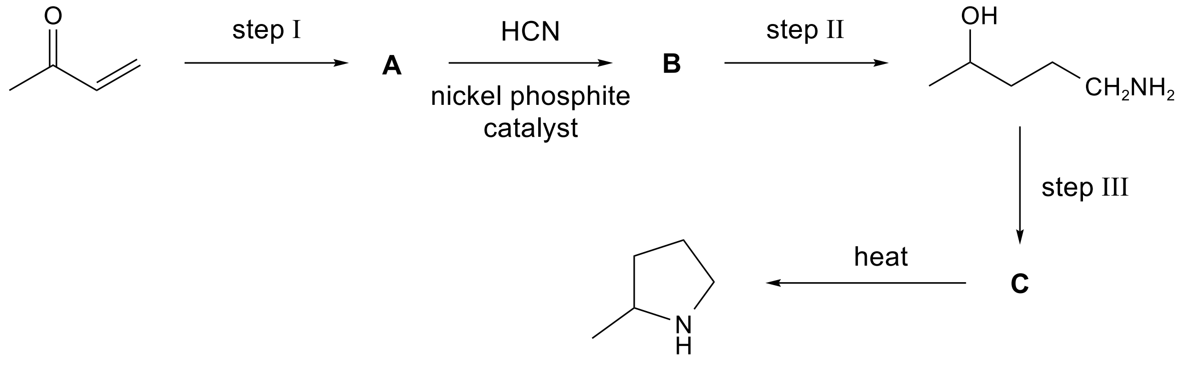
(d) Nickel is a useful catalyst for many organic reactions.

Hydrocyanation synthesizes alkyl nitriles from alkenes using nickel phosphite complexes as catalyst.

$$\mathrm{RCH{=}CH_2 + HCN} \xrightarrow{\text{nickel phosphite catalyst}} \underset{\text{alkyl nitrile}}{\mathrm{RCH_2CH_2CN}}$$

Butenone undergoes the following synthesis via an alkyl nitrile **B** to form neutral **F**.



F

(i) Draw the structures of **A**, **B** and **C** and describe the reagent and conditions needed for steps **I, II** and **III**. [6]

(ii) The equation below shows the combustion of butenone.

$$\boldsymbol{a}\ \mathrm{CH_3COCHCH_2} + \boldsymbol{b}\ \mathrm{O_2} \rightarrow \boldsymbol{c}\ \mathrm{CO_2} + \boldsymbol{d}\ \mathrm{H_2O}$$

Suggest values for the coefficients ***a***, ***b***, ***c*** and ***d***. [1]

(iii) Use appropriate data from the *Data Booklet* to calculate the enthalpy change of combustion of butenone. [2]

[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.